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Intrinsically Trapped Triplet Excitons in π -Conjugated Polymers

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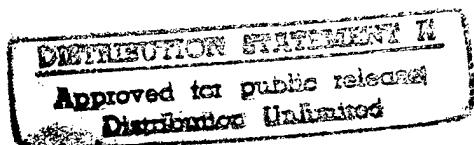
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Intrinsically Trapped Triplet Excitons in π -Conjugated Polymers

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The X-band spin 1 photoluminescence-detected magnetic resonance of frozen toluene solutions of poly(*p*-phenylene ethynylene) (PPE) and poly(*p*-phenylene)-type ladder (LPPP) polymers are presented. The amplitude of the 800 - 1100 G wide triplet resonance pattern decreases with decreasing concentration of PPE in toluene and tetrahydrofuran; in frozen saturated solutions of LPPP it is about half of that in neat films. The results suggest that the resonance is largely due to a long-lived (~30 μ s) trapped triplet exciton state localized on a phenylene ring and stabilized by coupling to a segment of an adjacent chain. The role of this trapped triplet in the photophysics of π -conjugated polymers is discussed.

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The triplet state in conducting polymers may be the most prolific of states generated by fusion of positive and negative carriers in π -conjugated polymer light-emitting diodes (LEDs) [1] but it is only poorly understood. The 25% theoretical upper limit of the electroluminescence (EL) quantum efficiency of the LEDs is derived from spin statistics, which should yield nonluminescent triplets in 75% of these fusion events. Triplet states are directly observed, albeit weakly, in biased polymer LEDs by EL- and conductivity-detected magnetic resonance [2-4]. The identification of these triplets with the ubiquitous states due to spin statistics is strongly suspected [4] but not firmly established. Therefore, a basic understanding of the behavior of the triplet states is highly desirable.

In this letter we describe the triplet photoluminescence (PL)-detected magnetic resonance (PLDMR) in powders and solutions of poly(*p*-phenylene) (PPP)-type ladder (LPPP) polymers (see inset of Figure 1) [5-7] and the 2,5-dibutoxy derivative of poly(*p*-phenylene ethynylene (PPE)) (DBO-PPE) (see inset of Figure 2) [8,9], which provide considerable insight into the nature of the triplet states. In frozen saturated solutions of m-LPPP the amplitude $\Delta I/I$ (i.e., the fractional change in the PL intensity I at the resonant field) of the triplet resonance is about half of that in films. In the DBO-PPE solutions it also decreases rapidly with decreasing concentration, from $\sim 1.4 \cdot 10^{-5}$ in saturated frozen solutions to $\sim 6 \cdot 10^{-6}$ in very dilute frozen solutions at 15 K. The results strongly suggest that the resonance is largely due to a long-lived ($\sim 30 \mu\text{s}$ in DBO-PPE films) triplet state localized on a single phenylene ring and stabilized by coupling to a segment of an adjacent chain. The nature of the sites which yield the remnant triplet resonance observed in the very dilute DBO-PPE solutions is also discussed.

The syntheses of the LPPPs and PPEs were described elsewhere [10,11]. The LPPPs exhibit relatively high intrachain order as manifest in the vibronic structure of their absorption spectra [5,6]. The methyl-substituted m-LPPP has the highest intramolecular order among the class of LPPPs [5,7]. While the relatively rigid structure of the PPEs suggest that they should also be well-ordered [8], their relatively broad and structureless PLDMR is actually consistent with considerable disorder [9].

The measured samples were prepared by dissolving the powders in toluene and vacuum sealing the solutions in quartz tubes. In each case the maximum concentration was that which showed no

visible precipitation at room temperature, i.e., the saturation concentration. The tubes were placed in the quartz finger dewar of an Oxford Instruments He gas flow cryostat, which is inserted in an optically accessible X-band microwave cavity. The PPEs and m-LPPPs were excited by the 488 and 457.9 nm lines of an Ar⁺ laser, respectively, at a laser power of less than 20mW. The PLDMR was measured by sweeping a DC magnetic field and amplifying the change in the PL signal with a lock-in amplifier referenced to the microwave chopping frequency ν_c . The triplet lifetimes, determined by monitoring the PLDMR vs ν_c , were measured with a fast photomultiplier tube while the magnetic field was fixed on the half-field triplet resonance. The cutoff frequency of the detection system was measured to exceed 100 kHz.

The PLDMR of π -conjugated polymer powders and films typically includes (i) a relatively strong 5-30 G-wide spin 1/2 polaron resonance at $g \approx 2.002$ and (ii) full- and (iii) half-field triplet exciton powder patterns which are due to the $\Delta m_s = \pm 1$ and ± 2 transitions, respectively, among the triplet sublevels [6,12-14]. The full-field triplet PLDMR patterns of films and frozen saturated toluene solutions of m-LPPP at $T = 15$ K are ~ 800 G wide (see Figure 1). The amplitude $\Delta I/I$ of the full-field triplet pattern is $\sim 4 \cdot 10^{-6}$ and $\sim 2 \cdot 10^{-6}$ in the films and frozen saturated solutions, respectively. The pattern is consistent with zero field-splitting parameters $D/g\beta \approx 630$ G and $E \approx D/3$, indicating absence of any axial symmetry and yielding [12] ~ 3 Å (the size of a phenyl ring) for the spatial extent of the triplet excitation [15,16]. Analysis of the half-field resonance (see inset of Fig. 1) resulted in the same values of D and E [17].

The full-field triplet resonance of a powder and frozen toluene solutions of selected concentrations of 2,5-dibutoxy PPE (DBO-PPE) at $T = 15$ K are shown in Figure 2. The full field triplet PLDMR pattern is ~ 1200 G wide in the powder, reflecting a localized triplet state whose extent is also slightly less than ~ 3 Å [13]. Note that the patterns are significantly broader than in m-LPPPs, suggesting that the extent of the triplet state is smaller in the PPEs. In addition, in the PPEs the patterns have gradually sloping wings which likely result from a wider distribution of D and E values than in the m-LPPPs. Analysis of the half-field resonance (see inset of Fig. 2) resulted in the same values of D and E in this case as well [9].

The shapes of the triplet patterns observed in the frozen toluene solutions are identical to that of the powder. Figure 3a shows that as the concentration of PPE increases from the very dilute limit,

$\Delta I/I$ remains constant until a concentration of ~ 0.09 mg/ml is reached. Above this concentration, $\Delta I/I$ increases up to the saturation concentration. The value of $\Delta I/I$ in the powder is $\sim 50\%$ higher than in the saturated solution. The behavior of the triplet resonance in tetrahydrofuran (THF) solutions was identical to the behavior in toluene.

Figure 3b shows that the dependence of the total PL intensity I is qualitatively different from that of $\Delta I/I$, peaking at a concentration of ~ 0.27 mg/ml. The decrease of I at low concentrations is due to the decreasing number of absorbing PPE molecules; the decrease at high concentrations is probably due to the increasing role of nonradiative decay paths associated with interchain coupling [6, 18], as radiative yields of π -conjugated polymer films are invariably lower than solutions.

Due to the relative weakness of the triplet resonance, the lifetime τ of the triplet state in PPE films determined by measuring the dependence of $\Delta I/I$ on the microwave chopping frequency v_c could only be roughly estimated. This estimate was obtained by fitting the modulus R of the lock-in output at the peak of the half-field resonance (see inset of Fig. 4) to the function

$$R = [1 + (2\pi v_c \tau)^2]^{-1/2} \quad (1)$$

Figure 4 shows the behavior of R vs v_c in DBO-PPE films at $T = 15$ K. The solid line is the behavior of Eq. (1) with $\tau = 30 \mu s$. The observed behavior is consistent with a nonradiative process with a distribution of lifetimes around this single value of τ [19]. It is qualitatively different from the behavior of the narrow spin 1/2 resonance of m-LPPP, poly(*p*-phenylene vinylenes) (PPVs), and poly(3-alkyl thiophenes) (P3ATs), which requires a model assuming at least two different lifetimes, one of which is in the millisecond range [6,20].

In assessing the significance of the results presented in this letter, we first note that previous room-temperature measurements on P3ATs dissolved in liquid CH_2Cl_2 yielded a polaron resonance but no triplet patterns [12,14,21]. These previous results were to be expected, since fast dynamical quenching of the triplets in liquids quenches their resonance. However, frozen solutions lock the molecules into a rigid host and therefore the foregoing mechanism should not apply. Therefore, the weakness of the triplet resonance in the frozen saturated m-LPPP solutions and its behavior vs concentration in the PPE solutions demands a different explanation. The

results clearly suggest a model requiring an interchain site such as a small trapped triplet exciton state that is spatially localized on a phenylene ring and stabilized by a unit of an adjacent chain. As discussed below, we believe that it is improbable that this state is a charge transfer triplet exciton.

As Fig. 3 indicates clearly, a remnant pattern with a concentration-independent value of $\Delta I/I$ persists in the dilute limit of frozen DBO-PPE solutions. It is unlikely that this pattern is due to triplet states stabilized by solvent-polymer coupling as the shape of the pattern in solutions would then differ from that in powders, in contrast to the experimental results. This is also confirmed by its identical behavior in THF and toluene solutions of DBO-PPE, since THF lacks π -bonds, in contrast to toluene. We consequently consider alternative possibilities: The remnant pattern is due to (i) some type of intrachain sites which stabilize the low-lying triplet state and (ii) interchain sites in aggregates, i.e. colloids or small bundles of molecules, that are present even in the dilute limit. Yet if the invariance of the shape of the triplet powder pattern rules out solvent-polymer coupling, it should also rule out intrachain sites. We also note that UV irradiation of PPE powders, which should induce crosslinking by elimination of π bonds and formation of σ bonds between adjacent units of neighboring chains, did not affect $\Delta I/I$ appreciably. We therefore propose that the remnant triplet resonance signal is due to triplets localized at sites similar to those in the films and concentrated solutions and associated with remnant aggregates or colloids which are present even in the dilute limit.

The picture of relatively long-lived triplets stabilized by adjacent polymer units provides additional insight into previous studies. The early PLDMR studies of P3AT [12] and PPV [13] films suggested that the degree of axial symmetry of the triplet states varied widely among the films and decreased rapidly with increasing temperature. At the same time, while the full- and half-field triplet patterns become increasingly structureless with increasing temperature, the overall width is temperature invariant. In addition, in the ordered state of PPV the phenylene units from one chain are proposed to be stacked adjacent to the vinylene units on the neighboring chains [22]. This interchain geometry is consistent with an essentially temperature independent distribution of D values, and values of E that increase with T. Thus, while isolated phenylene rings provide a symmetric ($E = 0$) environment for triplets, coupling with an adjacent vinylene, ethynylene, phenylene, or another bridging unit, and static and dynamical disorder lead to deviations from such

symmetry ($E > 0$).

We note that the foregoing model is supported by the behavior of C_{60} and C_{70} : In matrix isolated fullerene molecules, only the triplet state which is delocalized over the entire molecule is observable by light-induced ESR or PLDMR [23,24]. In fullerene films, however, the PLDMR includes an additional broad triplet pattern similar to that described in this letter and consequently believed to be localized on a face adjacent to a neighboring molecule [23,24]. It therefore appears that this long-lived triplet is an intrinsic trapped state of π -conjugated rings stabilized by coupling to a unit of an adjacent molecule or polymer.

The identification of the foregoing photoinduced intrinsically trapped triplet state with the source of the triplet PA band and the states resulting from the fusion of spin-parallel carriers in polymer LEDs [2-4] is not firmly established. We note, however, that the temperature dependence of the triplet PA band in CN-PPV is similar to that of the triplet PLDMR, and both are observable at higher temperatures than in typical PPVs [4]. Furthermore, there are no indications of additional triplet states in either the PLDMR or PA spectra. We therefore propose that the intrinsically trapped long-lived triplet states observed by PLDMR, those observed in polymer LEDs, and those responsible for the triplet-triplet PA band are essentially identical states. However, we expect that the spatial extent of the shorter-lived untrapped mobile triplet state of the ideal chain is greater than that of the trapped triplets observed by PLDMR.

Since the triplet resonance appears to result from triplets stabilized by coupling with a unit of an adjacent polymer, the possibility that it is an actual charge transfer triplet exciton should also be examined, but it is deemed unlikely: Such a state would differ qualitatively from the low-lying triplet state of the ideal isolated polymer or oligomer, whereas the state localized on a ring and stabilized by coupling with an adjacent unit could be similar to that of the ideal isolated polymer, but of slightly lower energy.

Finally, we note that the mechanism yielding the triplet PLDMR had previously been assigned to spin-dependent triplet-triplet fusion to singlets [12,13]. This mechanism, however, is problematic since it should result in delayed fluorescence in the 10 - 100 microsecond time range. Such delayed fluorescence, however, has not been detected to date, and the resonance is suggested to result from the role of triplets as nonradiative singlet quenching centers [4,6] and/or ground-state

repopulation [25]. We speculate that these triplets and the long-lived interchain polaron pairs described by Graupner et al. [6] might be a very significant source of the well-known "solid state effect," namely the reduced PL yield of polymer films as compared to solutions.

In summary, the photoluminescence-detected magnetic resonance spectra of frozen toluene solutions of methyl-substituted poly(*p*-phenylene)-type ladder polymers and derivatives of poly(*p*-phenylene ethynylene) suggests that the triplet state is an intrinsic long-lived (~30 μ s in PPEs) trapped state localized on a phenylene ring and stabilized by coupling to a unit of an adjacent chain.

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Figure Captions

Figure 1. The full-field PLDMR of films (solid line) and frozen saturated solutions (dashed line) of m-LPPP at $T = 15$ K. Note the intense spin 1/2 polaron resonance and the absence of the broad triplet powder pattern in the saturated solution of m-LPPP in toluene. Insets: The molecular structure of LPPPs, where $Y = \text{CH}_3$, $R = \text{C}_{10}\text{H}_{21}$, and $R' = \text{C}_6\text{H}_{13}$, and the half-field triplet PLDMR pattern.

Figure 2. The full-field PLDMR of a powder (solid line) and frozen toluene solutions of selected concentrations of 2,5-dibutoxy PPE (DBO-PPE) at $T = 15$ K: Dashed, dashed-dotted, and dotted lines are 0.5, 0.27, and 0.09 mg/ml, respectively. Note the intense spin 1/2 polaron resonance and the behavior of the broad triplet powder pattern. Insets: The molecular structure of DBO-PPE and the half-field triplet PLDMR pattern..

Figure 3. The amplitude $\Delta I/I$ of the half-field triplet resonance and the PL intensity I vs concentration of DBO-PPE in toluene at $T = 15$ K. The values for DBO-PPE powder are shown at the equivalent concentration of 1000 mg/mL. The lines are a guide to the eye.

Figure 4. The observed behavior of the modulus R of the lockin amplifier, proportional to the amplitude $\Delta I/I$ of the half-field triplet PLDMR in PPE films, vs the microwave chopping frequency v_c at $T = 15$ K.

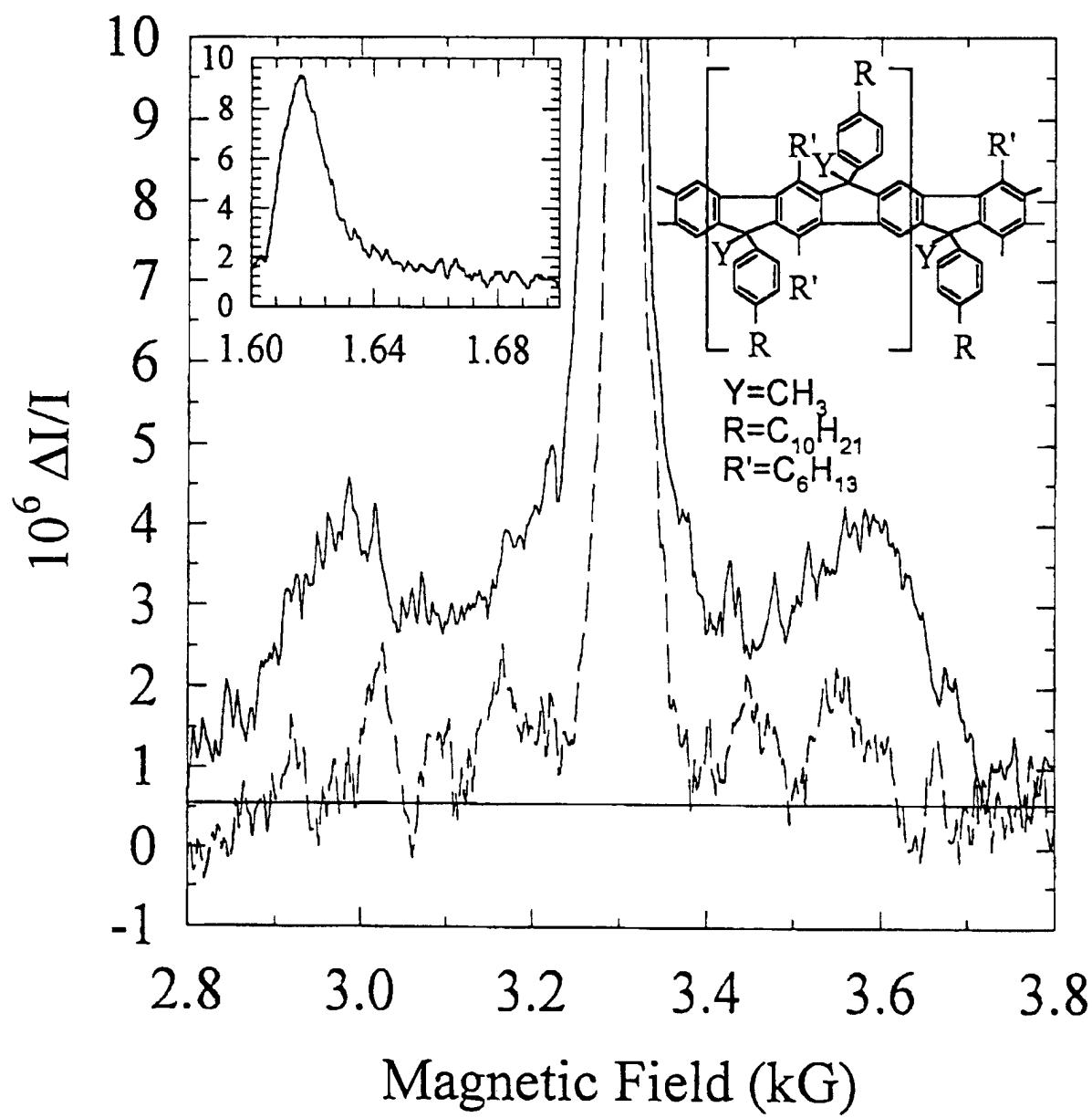


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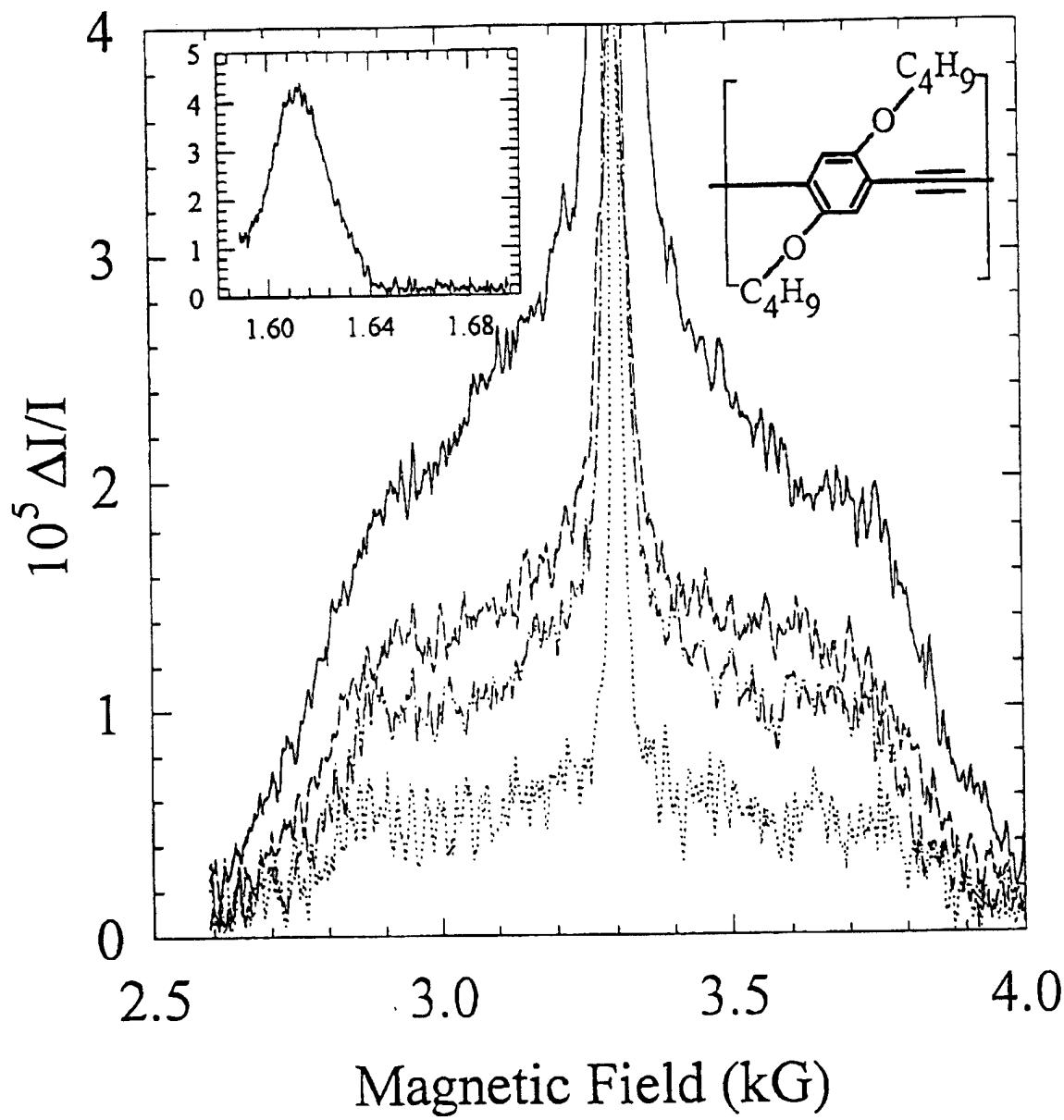


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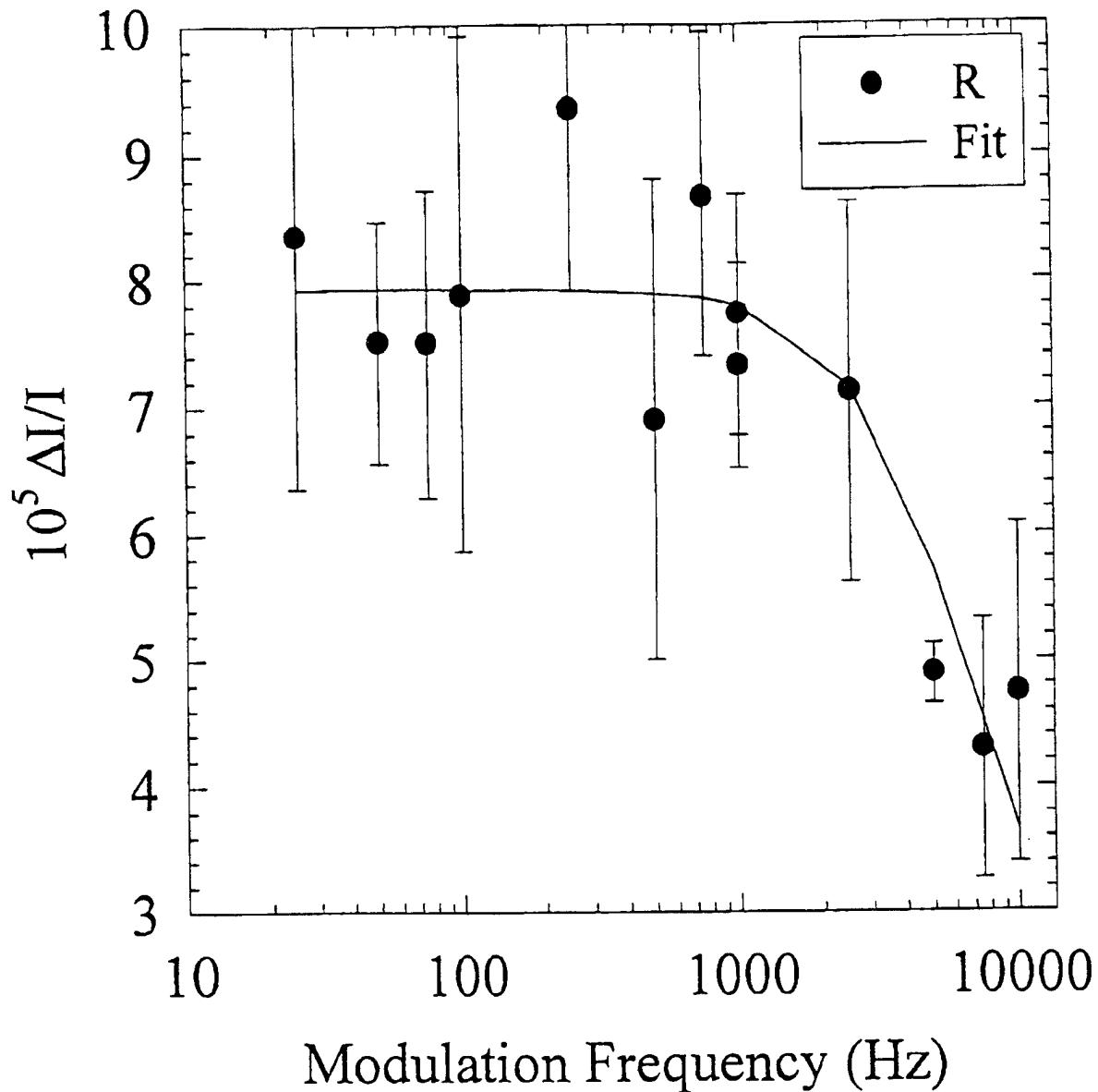


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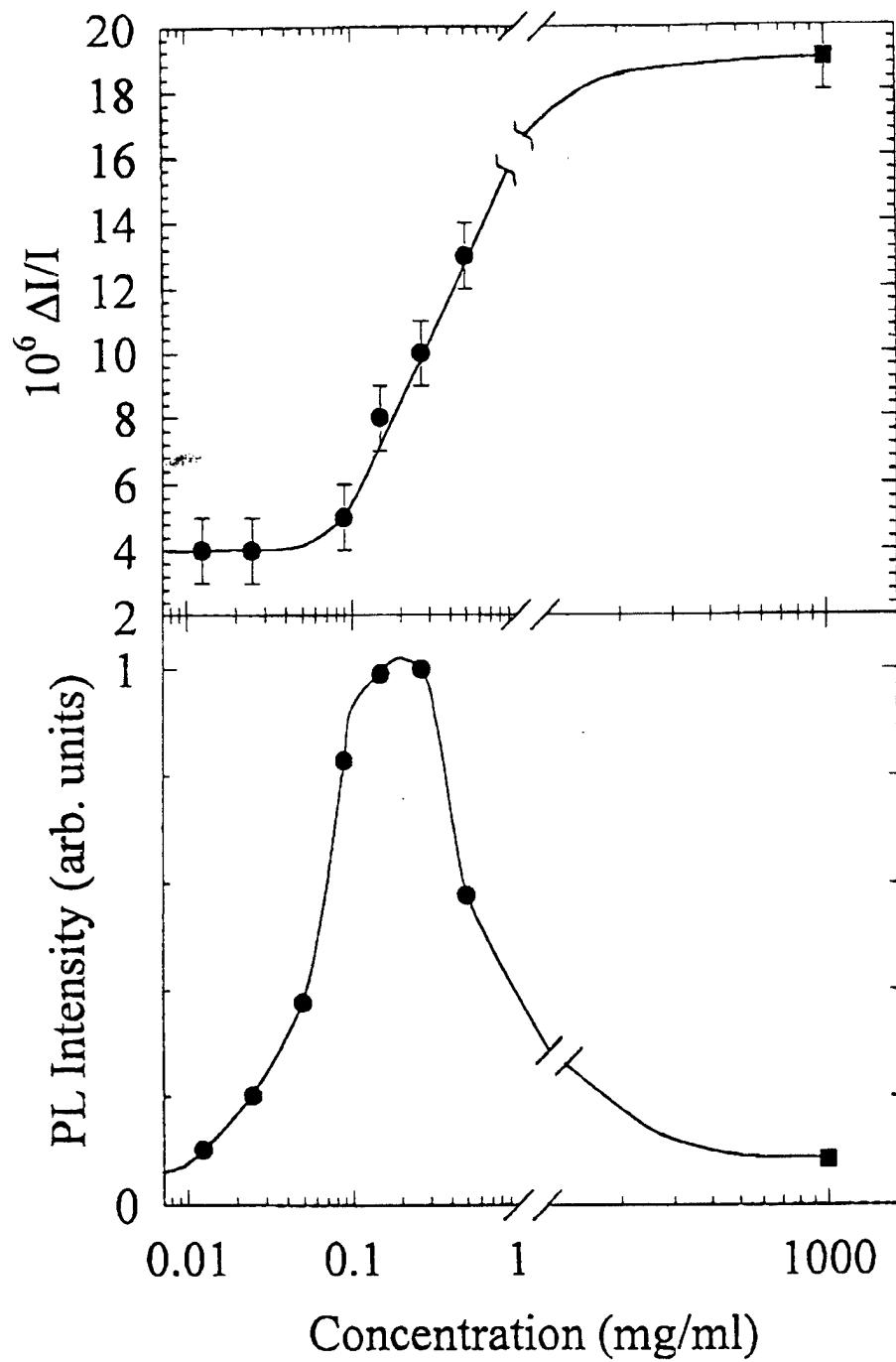


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